THE RELATION BETWEEN THE QUANTITIES OF TIN AND HYDROGEN IN "SPRINGERS."

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A SEARCH of the literature available on this subject reveals very little from a bacteriological standpoint and not a great deal from a chemical point of view.

A gas-producing organism having the characteristics of *B. putrificus coli* was isolated from "swells" containing meat by Fowler in 1908[1].

Tonney and Grooken[2] attributed the presence of carbon dioxide and alcohol in canned goods to alcoholic fermentation, which occurs as a result of imperfect sterilization. The presence of nitrogen they attributed to protein decomposition, claiming that the amount of this gas is an index of the amount of such decomposition. They found hydrogen present in amounts varying from none to 48 percent. Its presence was an indication of ptomaine-producing substances. Marsh gas, which occurred in small amounts, had the same significance. Carbon monoxide, which occurred occasionally, was formed by the reduction of carbon dioxide by nascent hydrogen. Oxygen, occurring in traces only, was present as a constituent of air. They found extreme variations in the kinds and amounts of gases in the same types of foods.

J. M. Coerbergh[3], working with canned spinach, found that the amount of tin in material put up in cans, by the same maker and at the same time, may vary greatly. The amount in unvarnished cans one year old was less than 126 mgs. per kilogram of food, while the amount in varnished cans was always much less. He found that the amount of tin bore no relation to the amount of air or of nitrates in the cans.

R. F. Bacon, in an article entiled "Tin Salts in Canned Goods of Low Acid Content"[4], states that many nonacid foods attack tin linings to a very marked extent. A determination of the ratio of tin to acid in a number of canned foods showed that this ration was highest in nonacid vegetables and lowest in acid

1. Third Report of the Committee on Physiological Effects of Food, Training and Clothing on the Soldier, 1908, 49-51.
2. "Analysis of Gases Contained in Swollen Canned Goods," American Food Journal 3, 1908.
3. Pharm. Weekblad 49, 429-31, 490-495, Chem. Abs. 1912.
4. U. S. Dept. Agri., Bur. Chem., Circular 79, 1911.

fruits and vegetables. He found that shrimps contain a corrosive substance which attacks tin vigorously. The compound $N(CH_3)H_2$ isolated from this product dissolved tin slowly. He investigated the action of several alkaline substances, amino acids and purine bases, and found that many of these substances would dissolve tin in considerable quantities. His conclusion was that the action of nonacid foods was due to amines and amino acids.

W. Rossee and Von Morgenstern, in an article entitled "Abnormal Amounts of Tin in Canned Foods,"[5] state that canned foods always contain some tin removed from the receptacle, but usually only small amounts. Large amounts are dissolved when the can is left open for some time. Canned spinach, originally containing 18 mgs. of tin, after six days' exposure contained 1,038 mgs. per kilo. Similar results were obtained with other vegetables. They state that the tin forms insoluble compounds with the vegetable substance, and is not redissolved by the gastric juice. Their conclusion is that the small amounts of tin usually found in canned foods are not to be considered injurious.

H. A. Baker, in his article, "The Disappearance of Oxygen in Canned Food Containers,"[6] states that the gases in the head space of "springers" are never more than three—carbon dioxide, nitrogen and hydrogen. He defines the term "springer" as "a trade name given to cans with bulging ends, which contain perfectly sound and sterile food products." The source of these gases he states as follows:

Carbon dioxide is produced during the time of processing, and may be produced in excessive amounts if the time from the beginning of the preparation of the material to the period of sterilization is not short.

Nitrogen is present as a residue from unremoved air.

Hydrogen is present as a result of the action of fruit and vegetables acids on metallic containers.

The disappearance of the oxygen originally present as a constituent of the air left in the head space of the container he attributes to at least three causes, as follows:

(*a*) It may combine with the metals tin and iron, forming oxides.

5. Z. offentl. Chem. 20, 171-172, 1914.
6. Original Communication, Congress of Applied Chemistry, vol. 18, 1912.

(*b*) It may be used up in the oxidation of salts of these metals.

(*c*) It may combine with nascent hydrogen.

(*d*) It may combine with fatty materials during processing.

A. W. Bitting, in "Methods Followed in the Commercial Canning of Foods,"[7] states: "It is always possible to tell a 'swell' from a 'springer' by the use of a microscope, as in the former there will be large numbers of organisms, while in the latter there will be very few." It will be inferred from this statement that cans which are "bulged" only as a result of the presence of hydrogen formed by the action of acids on tin are to be considered as "springers."

W. D. Bigelow, in the September, 1916, *Journal of Industrial and Engineering Chemistry,* points out that tin in canned food is largely, sometimes chiefly, in the form of insoluble compounds; that the acid acts as a carrier of tin from the coating of the container to the food material.

In the November *Journal* the same author states that with nonacid foods such as peas or corn, swells are usually due to decomposition. On the other hand, spoilage rarely occurs with acid fruits unless the can be leaky. In this class of products swelling of the can is almost invariably due to hydrogen set free by the action of the fruit acid on the metal of the container.

This review of the literature on the subject shows that no work has been done on "springers" and "swells" involving the quantitative determination of tin and the various gases. It seemed desirable, therefore, to secure some data of this nature.

If the hydrogen present in canned foods is the product exclusively of the action of acids on the tin of the container, then obviously there should be a definite relation between the amounts of tin and hydrogen present. If the hydrogen is partially the product of the action of acid on other metals of the container, such as iron, then the hydrogen present should be greater in quantity than that capable of being liberated by the tin present. To obtain information in regard to this matter, determinations were made for tin and the various gases in eighty-three samples of bulged canned goods. These represent the following products: corn, pumpkin, sweet pota-

7. U. S. Dept. Agri., Bul. 196, 1915.

toes, greens, tomatoes, peaches, apples, hominy, beets, kraut, asparagus, blackberries, raspberries, strawberries and cherries. The tables appended contain the results obtained. For the sake of ready comparison the tin is expressed in milligrams per kilogram of food and the gases as cubic centimeters per kilogram.

The term "excess gas," as used in the tables, is to be interpreted as meaning the amount of gas given off by the can during the equalization of pressure.

The volume of gas remaining in the can was obtained from measurements of the total volume of the can and the volume of the food contents.

The tin determinations were made by the iodine titration method, as outlined by H. A. Baker in his article "Special Adaptation of Iodine Titration Methods for the Estimation of Tin, Especially in Connection with Determinations of 'Salts of Tin' in Canned Foods," published in "Original Communications, Congress of Applied Chemistry."

An examination of the table will show that:

1. In the majority of cases the gases present were hydrogen, carbon dioxide, and nitrogen (the inactive residual gas being considered as nitrogen). The presence of these three gases alone, coupled with the fact that the condition of the food in 90 percent of the samples was good, judged by the taste, smell and appearance, suggests that the samples examined were "springers."

2. No definite relation exists between the amounts of tin and hydrogen.

3. The hydrogen in nearly all cases is a small fraction of the amount which the tin present is capable of liberating by interaction with acids.

These facts suggest that considerable tin is corroded by agents other than acids.

4. The amounts of carbon dioxide present in the majority of samples are relatively large. Whether these amounts are formed during processing, or subsequently as a result of fermentation, has not been determined.

5. There is a wide variation in the amounts of tin and gases in the various kinds, and also in the same kind of foods.

Amounts of tin and gases in bulged canned goods.

Contents, grams.	Excess gas, cc.	Total gas, cc.	Tin per kilo, mgs.	Gases per kilogram of fruit.		
				Total cc.	Hydrogen cc.	Carbon dioxide cc.
			CORN.			
603	100*	170*	79	281	11	185
617	83	163	45	264	169	144
595	41	116	265	194	91	61
585	25	115	34	196	6	27
			PUMPKIN.			
957	87	167	822	175	6	161
			SWEET POTATOES.			
588	22	....	158	....	Present	Present
546	74	....	292	....	Present	Present
			GREENS.			
762	....	....	213	....	Present	Present
773	100*	100*	339	....	Present	Present
			TOMATOES.			
588	7	42	117	71	....	19
843	52	77	93	91	58	16
			PEACHES.			
....	70	329	324	....	....	Present
840	29	129	163	154	97	3
840	45	135	91	158	83	5
840	65	225	109	267	180	8
812	63	173	245	213	122	6
883	5	150	113	....	....	....
843	1	....	163	....	....	....
826	21	96	185	116	18	....
			MOLASSES.			
1112	100*	....	53	....	....	Present
			APPLES.			
720	....	....	538	....	....	....
			HOMINY.			
964	100*	100*	38	....	Present	Present
1000	....	....	53	....	....	....
			BEETS.			
957	100*	100*	186	....	Present	Present
			KRAUT.			
953	45	90	56	94	3	27
			ASPARAGUS.			
937	....	....	320	....	....	....

* Not a swell.

Amounts of tin and gases in bulged canned goods—concluded.

Contents, grams.	Excess gas, cc.	Total gas, cc.	Tin per kilo, mgs.	Gases per kilogram of fruit.		
				Total cc.	Hydrogen cc.	Carbon dioxide cc.
			BLACKBERRIES.			
....	85	....	386	....	Present	Present
528	27	82	380	155	97	16
588	45	100	520	170	91	13
567	36	116	490	204	54	42
588	97	172	918	293	236	52
542	41	111	170	214	134	52
581	37	102	485	176	96	30
557	54	144	543	259	163	63
546	41	136	626	249	156	88
578	23	83	490	144	64	18
....	33	....	427	....	Present	Present
588	77	152	779	266	185	33
588	38	113	508	192	124	18
581	44	99	371	167	109	13
592	100*	100*	927	....	Present	Present
581	30	90	684	155	102	21
588	24	79	455	134	58	20
539	36	141	722	262	174	31
581	59	119	605	205	135	16
576	....	....	332	....	....	....
....	43	....	251	....	Present	Present
578	29	64	421	111	53	18
576	37	77	254	133	68	22
....	55	....	454	....	Present	Present
588	52	107	430	182	118	20
576	28	88	406	152	87	20
560	....	....	226	....	....	....
576	....	....	347	....	....	....
....	....	....	96	....	....	....
570	28	58	55	109	81	9
546	75	120	31	219	206	12
581	47	82	107	141	25	9
613	62	100	194	163	124	8
585	54	99	335	169	142	9
578	....	....	475	....	....	....
563	40	110	633	195	99	30
576	....	....	294	....	....	....
574	4	69	311	....	....	....
			RASPBERRIES.			
....	....	....	219	....	....	....
617	41	86	126	140	92	19
549	43	133	84	242	160	24
617	58	93	59	151	130	11
617	43	83	127	135	108	12
599	106	161	428	269	191	16
549	....	....	274	....	Present	Present
599	41	76	360	127	75	9
606	25	50	594	83	57	6
539	17	105	153	195	157	17
			STRAWBERRIES.			
574	59	104	133	181	19	27
602	36	76	147	124	53	22
			CHERRIES.			
921	43	93	461	101	62	8
602	3	38	146	....	....	....
588	28	78	178	132	....	7
613	Leaking	....	117	....	....	....
492	Leaking	....	110	....	....	....
620	16	36	221	57	39	3
634	3	28	105	....	....	....

* Not a swell.

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